

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 December 2001 (20.12.2001)

PCT

(10) International Publication Number
WO 01/96621 A1

(51) International Patent Classification⁷: **C22B 3/26, 3/38, 3/40, 19/00, 23/00**

(74) Agent: **GRIFFITH HACK**; 168 Walker Street, NORTH SYDNEY, New South Wales 2060 (AU).

(21) International Application Number: **PCT/AU01/00696**

(22) International Filing Date: **13 June 2001 (13.06.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
PQ 8127 13 June 2000 (13.06.2000) AU

(71) Applicant (for all designated States except US): **WMC RESOURCES LIMITED [AU/AU]; 37TH FLOOR, QV1 BUILDING, 250 ST GEORGES TERRACE, PERTH, Western Australia 6000 (AU).**

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

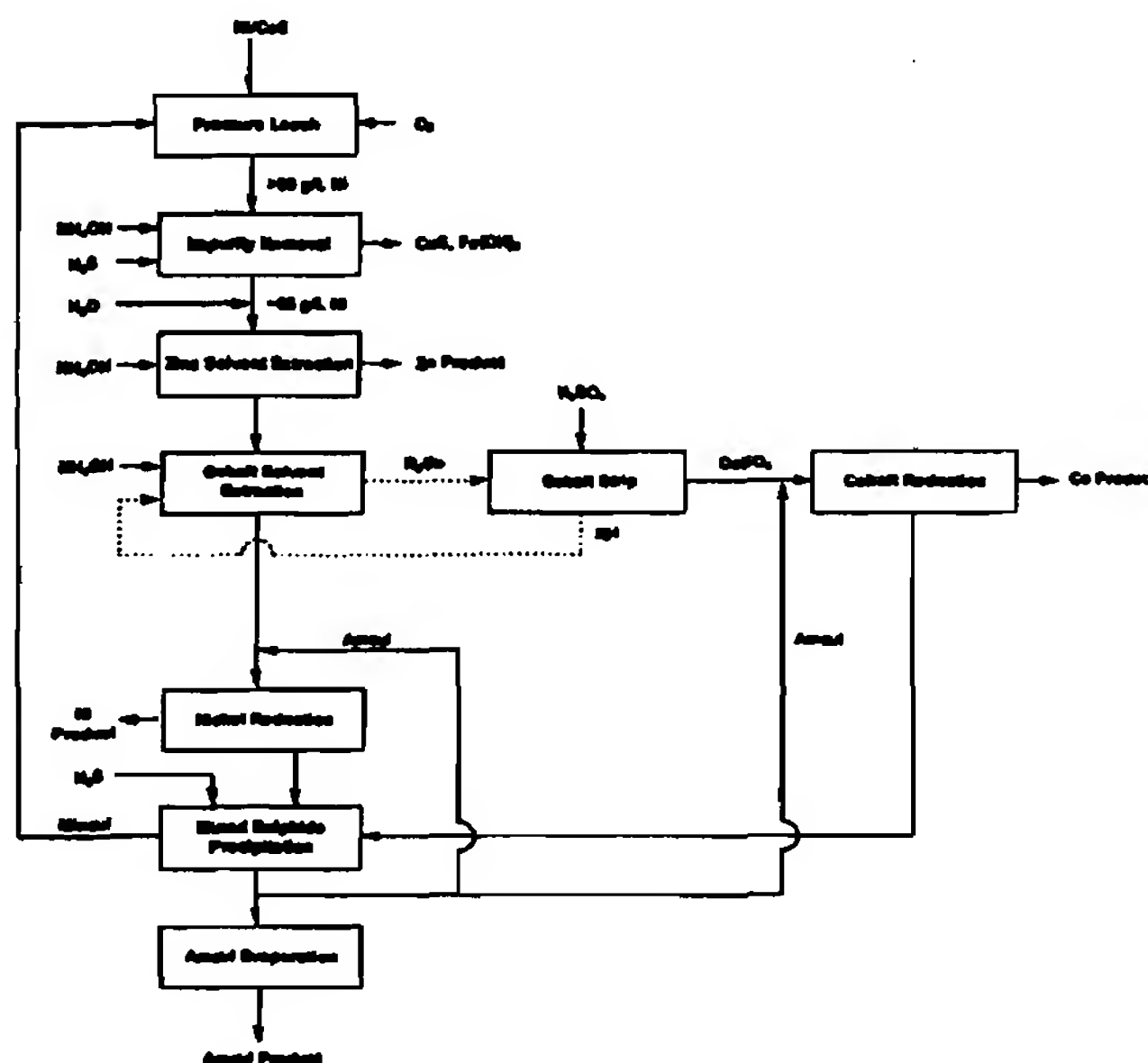
(75) Inventors/Applicants (for US only): **O'CALLAGHAN, John [AU/AU]; 24 Mason Road, KALAMUNDA, Western Australia 6076 (AU). CHAMBERLAIN, Anthony [AU/AU]; 12 Aldinga Street, KENWICK, Western Australia 6107 (AU).**

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **SOLVENT EXTRACTION OF IMPURITIES FROM CONCENTRATED METAL SULPHATE SOLUTIONS**



(57) Abstract: The present invention relates generally to a two step solvent extraction circuit to remove impurity metals of zinc and cobalt selectively from a valuable metal of nickel. In order to selectively extract zinc there must be sufficient separation between zinc and cobalt in the cyanex 272 system. Similarly for cobalt and nickel, the separation factor must be of sufficient magnitude to obtain a pure nickel product. The process for the solvent extraction of impurity metals is operated at a temperature exceeding 60°C being the maximum temperature at which solvent extraction circuits conventionally operate.

SOLVENT EXTRACTION OF IMPURITIES FROM CONCENTRATED METAL SULPHATE SOLUTIONS

FIELD OF THE INVENTION

5 The present invention relates generally to a method of removing impurity metals from an impure valuable metal sulphate stream in a solvent extraction circuit. More particularly, the invention relates to the extraction of cobalt and/or zinc from a concentrated nickel sulphate
10 liquor.

BACKGROUND TO THE INVENTION

In the processing of nickel laterites, nickel and cobalt are selectively separated from a wide range of impurities
15 by mixed (Ni/Co) sulphide precipitation. This mixed sulphide is then re-leached using temperature and oxygen over pressure. The resulting leach solution is acidic and usually has concentration ranging from 60 - 120 g/L nickel and 5 -15 g/L cobalt, together with other impurities like
20 copper and zinc. Similarly concentrated leach solutions can also be obtained from the pressure leaching of nickel sulphide concentrates with oxygen. After neutralisation of the acid cobalt can then be separated from nickel via solvent extraction. Cyanex 272 is typically used to
25 selectively extract cobalt over nickel in a sulphate matrix at a fixed pH. However the extraction of cobalt is a cation exchange reaction which releases protons from the reagent which must be neutralised as this extraction is pH sensitive. Ammonia is typically used as the neutralising
30 solution both to raise the pH prior to solvent extraction, and to maintain a constant pH during extraction. The main problem with the use of ammonia in this instance is the precipitation of nickel ammonium sulphate, more commonly known as nickel double salts, when dealing with solutions
35 containing high nickel and ammonium sulphate

- 2 -

concentrations. For this reason, the feed solution is usually diluted to 50-70 g/L nickel strength to prevent the formation of nickel double salts.

5 Figure 1 is a conventional process flowsheet for refining a mixed sulphide showing the extraction of cobalt from a nickel sulphate solution with a direct addition of ammonia to a cobalt solvent extraction circuit. The direct addition of ammonia to the concentrated nickel sulphate
10 solution results in the formation of insoluble nickel ammonium sulphate double salts.

Australian patent No. 667539 by Outokumpu describes a two stage process which avoids the formation of this double
15 salt by:

- (i) pre-neutralisation of a cationic extractant such as Cyanex 272 to form the ammonium salt; and
- (ii) pre-extraction or exchange of the Cyanex 272 ammonium salt with magnesium sulphate in an aqueous solution
20 to form a Cyanex 272 magnesium salt which is contacted with an aqueous nickel sulphate solution in a solvent extraction circuit so as to extract nickel.

Another means of avoiding double salt formation is
25 described in the specification of the applicant's International patent application No. PCT/AU98/00457. This avoids the relatively expensive two stage pre-equilibration proposed by patent No. 667539 by adding chemically reactive magnesia, magnesium hydroxide, or
30 magnesium carbonate to the cationic extractant without the pre-neutralisation step. However, if magnesia or magnesium pre-equilibrated extractant is used to avoid the formation of double salts this introduces magnesium ions that contaminates the final ammonium sulphate product.

- 3 -

SUMMARY OF THE INVENTION

According to the present invention there is provided a method of removing impurity metals from an impure concentrated valuable metal sulphate stream in a solvent extraction circuit, said method involving contacting the impure concentrated valuable metal sulphate stream with a cationic solvent extractant, in the solvent extraction circuit operated at a relatively high temperature which is effective in increasing the solubility of the valuable metal in the concentrated sulphate stream containing ammonium sulphate, said extraction circuit also being operated whereby one or more of the impurity metals is loaded on the cationic solvent extractant using ammonia to control the pH whilst a raffinate of the solvent extraction circuit which contains the valuable metal is enriched in ammonium sulphate.

Conventionally when ammonia serves as the neutralising agent with concentrated nickel sulphate liquors, insoluble nickel salts such as nickel ammonium sulphate double salts may be formed. According to an embodiment of the invention, the formation of insoluble valuable metal salts is avoided by operating the solvent extraction circuit at significantly higher temperatures than is conventionally practised, and by using kerosene diluents with significantly higher flash point temperatures.

Generally the impure valuable metal sulphate stream is a nickel sulphate liquor, for example that obtained by acid/oxygen pressure leaching of a nickel-cobalt sulphide concentrate or a mixed nickel/cobalt sulphide precipitate obtained during the processing of nickel lateritic ores.

Preferably the relatively high temperature is greater than about 60°C. More preferably the high temperature is between about 80 to 100°C.

Typically the nickel sulphate liquor is a relatively concentrated liquor. More typically the nickel sulphate liquor contains at least about 60 g/L Ni.

5

Preferably the cationic solvent extractant is mixed with an organic diluent of a relatively high flash point. More preferably the organic diluent is a paraffin based diluent such as that commercially available as ISOPAR V.

10

Typically the solvent extraction circuit is designed to remove one or two of said impurity metals, respectively, from the nickel sulphate liquor. More typically two extraction circuits are designed to remove Zn and Co, respectively, from the nickel sulphate liquor.

15

Preferably the cationic solvent extractant comprises a phosphinic acid such as a bis (2,4,4 trimethylpentyl) phosphinic acid, for example that commercially available as CYANEX 272.

20

Generally the impurity metals include Co, Zn, Fe, Al, Cr and Cu.

25 BRIEF DESCRIPTION OF THE DRAWINGS

In order to achieve a better understanding of the nature of the present invention, a preferred embodiment of a method of removing impurity metals from an impure concentrated valuable metal sulphate stream in a solvent extraction circuit will now be described, by way of example only, with reference to the following drawings:

30

Figure 1 is a conventional refinery flow sheet for treating nickel sulphate leach liquors;

35

Figure 2 is a two stage zinc/cobalt solvent extraction recovery circuit;

Figure 3 is a pH extraction isotherm at a temperature of 85°C for Cyanex 272 in a preferred high flash point

- 5 -

temperature diluent using an impure concentrated nickel sulphate liquor;

Figure 4 is a comparative pH extraction isotherm at 50°C for Cyanex 272 in Shellsol 2046 kerosene diluent for an impure nickel sulphate liquor; and

Figures 5 to 8 are nickel solubility plots at 50°C, 60°C, 70°C and 80°C which show the relative solubility of a range of nickel sulphate solutions in the presence of various ammonium sulphate concentrations.

10

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

According to one embodiment of a process for the solvent extraction of impurity metals from a concentrated nickel sulphate liquor the solvent extraction circuit is operated at a temperature exceeding 60°C being the maximum temperature at which solvent extraction circuits conventionally operate. This is now feasible with the availability of high flash point diluents and the commercialisation of pulse columns. This will for example enable the conventional process flowsheet shown in Figure 1 to be operated at high nickel strengths and avoid dilution of the nickel process stream prior to cobalt removal. It has been found in one embodiment that by operating the solvent extraction circuit at 85°C ammonium sulphate concentrations above 50 g/L can be tolerated at nickel strengths of 90 - 100 g/L.

A cationic solvent extractant Cyanex 272 (a phosphinic acid), was used in this example together with an isoparaffin diluent ISOPAR V. An impure valuable metal sulphate stream in this example is a nickel sulphate liquor which was produced from pressure leaching a mixed sulphide which in turn had been produced by treating a

30

- 6 -

nickel laterite leach liquor with hydrogen sulphide. The liquor composition is shown in Table 1.

Table 1 - Impure Nickel Sulphate Solution Composition (g/L)

Ni	Co	Zn	Cu	Mn	Fe	Cr	Ca	Al	S	Amsul
103	8.78	0.634	0.002	0.012	0.246	0.063	0.060	0.082	68.0	21.7

5

Cyanex 272 extractant is a phosphinic acid that is highly selective in the separation of zinc and cobalt from nickel. When in its protonated form (H^+) the pH decreases
 10 as the zinc or cobalt is extracted and exchanges with the hydrogen ion according to the following reaction:



15 where, $M = Zn$ or Co .

The acid generated from the reaction is neutralised with ammonia to form ammonium sulphate.

20 Figure 2 shows a two step solvent extraction circuit to remove impurity metals of zinc and cobalt selectively from a valuable metal of nickel. In order to selectively extract zinc there must be sufficient separation between zinc and cobalt in the Cyanex 272 system. Similarly for
 25 cobalt from nickel, the separation factor must be of sufficient magnitude to obtain a pure nickel product. The separation factor is dependent on a number of variables including temperature, aromatic content of diluent, and extractant concentration. In the case of nickel hydrogen
 30 reduction up to 2 g/L cobalt can be present in the nickel reduction feed without causing any significant technical issues. In the case of nickel electrowinning less than

- 7 -

10ppm cobalt can be present in the nickel catholyte to result in the production of off-spec LME nickel.

The extraction pH isotherms were constructed to determine the optimum operating pH during extraction. Figure 3 shows the pH extraction isotherm according to one embodiment of the invention obtained at a temperature of 85°C for 0.85M Cyanex 272 in ISOPAR V using a concentrated feed solution containing about 103 g/L Ni and 9 g/L Co. Figure 4 shows a comparative pH extraction isotherm for 0.45M Cyanex 272 in Shellsol 2046 obtained at 50°C using the impure feed solution diluted to a nickel concentration of 65 g/L. As mentioned above the separation factor of Cyanex 272 is dependent on the temperature of the extraction and the aromatic content of the diluent. The two extraction isotherms of Figures 3 and 4 indicate a shift to the left with an increase in temperature and lower aromatic content of the diluent according to the preferred method of the invention.

20

The bench scale tests indicated that selective extraction of zinc over cobalt is possible with Cyanex 272. It is envisaged that this stage will be controlled between pH 2.00 and 2.25. A certain amount of zinc can be tolerated in the cobalt and nickel reduction feed. This zinc would be precipitated at the end of hydrogen reduction as a mixed sulphide. It is anticipated that any co-extracted cobalt will be recovered in the scrub circuit and recycled to extraction as shown in Figure 3.

30

Cobalt can be selectively extracted from nickel in the pH range of 4.00 to 4.50. Any Fe, Cu, Zn, Mn and Mg remaining in the liquor will be fully loaded onto the

- 8 -

organic with the cobalt. However, these impurities should be present at very low levels.

Figures 5 to 8 are plots of the relative nickel solubility over a range of nickel concentrations in the presence of various concentrations of ammonium sulphate at selected temperatures. Figures 5 and 6 are intended as comparative plots at the maximum normal operating temperatures for solvent extraction and show significant precipitation of nickel occurs once the concentration of Ni exceeds 60 g/L in the presence of more than 40 g/L ammonium sulphate. Figures 7 and 8 give an indication of nickel solubility at temperatures within the scope of the preferred embodiment of the present invention. It is clear that the increased temperatures increase the solubility of the valuable metal, in this example nickel, with relatively high concentrations of ammonium sulphate. For example, at 80°C an ammonium sulphate concentration of 50 g/L can be tolerated at nickel strengths of between 80 to 120 g/L.

20

Now that a preferred embodiment of the invention has been described in some detail it will be apparent to those skilled in the art that the method of removing impurity metals in a solvent extraction circuit has at least the following advantages:

25

- (i) increased concentrations of nickel can be tolerated in the solvent extraction circuit; and
- (ii) relatively high temperatures for the extraction circuit are possible with high flash point diluents.

30

Those skilled in the art will appreciate that the invention described herein is susceptible to variations

- 9 -

and modifications other than those specifically described. For example, the impure valuable metal sulphate stream may be cobalt sulphate and is not limited to the concentrated nickel sulphate liquor described. Furthermore, the
5 temperature of the extraction circuit need not be restricted to the temperatures described but rather extend to relatively high temperatures that are effective in increasing the solubility of the valuable metal in the sulphate stream in the presence of added ammonium
10 sulphate. The cationic solvent extractant and diluent described may also vary provided the required impurity metal loading is achieved.

All such variations and modifications are to be considered
15 within the scope of the present invention the nature of which is to be determined from the foregoing description.

It is to be understood that a reference herein to a prior art document does not constitute an admission that the
20 document forms part of the common general knowledge in the art in Australia or in any other country.

25

30

- 10 -

CLAIMS:

- 1) A method of removing impurity metals from an impure concentrated valuable metal sulphate stream in a solvent extraction circuit, said method involving contacting the impure concentrated valuable metal sulphate stream with a cationic solvent extractant, in the solvent extraction circuit operated at a relatively high temperature which is effective in increasing the solubility of the valuable metal in the concentrated sulphate stream containing ammonium sulphate, said extraction circuit also being operated whereby one or more of the impurity metals is loaded on the cationic solvent extractant using ammonia to control the pH whilst a raffinate of the solvent extraction circuit which contains the valuable metal is enriched in ammonium sulphate.
- 2) A method as defined in Claim 1 wherein the relatively high temperature is greater than about 60°C.
- 3) A method as defined in Claim 1 wherein the high temperature is between 80 to 100°C.
- 4) A method as defined in any one of the preceding claims wherein the impure valuable metal sulphate stream is a nickel sulphate liquor.
- 5) A method as defined in Claim 4 wherein the nickel sulphate liquor is obtained by acid/oxygen pressure leaching of a nickel/cobalt sulphide precipitate obtained during the processing of nickel lateritic ores.

- 11 -

- 6) A method as defined in Claim 4 or 5 wherein the nickel sulphate liquor is a relatively concentrated liquor.
- 5 7) A method as defined in Claim 6 wherein the nickel sulphate liquor contains at least about 60 g/L Ni.
- 8) A method as defined in any one of Claims 4 to 7 wherein the solvent extraction circuit is designed to
10 remove one or two of said impurity metals, respectively, from the nickel sulphate liquor.
- 9) A method as defined in Claim 8 wherein two extraction circuits are designed to remove Zn and Co, respectively,
15 from the nickel sulphate liquor.
- 10) A method as defined in any one of the preceding Claims wherein the cationic solvent extractant is mixed with an organic diluent of a relatively high flash point.
20
- 11) A method as defined in Claim 10 wherein the organic diluent is a paraffin based diluent.
- 12) A method as defined in any one of the preceding
25 Claims wherein the cationic solvent extractant comprises a phosphonic acid such as a bis (2,4,4 trimethylpentyl) phosphonic acid.
- 13) A method as defined in any one of the preceding
30 Claims wherein the impurity metals include Co, Zn, Fe, Al, Cr and Cu.

1/8

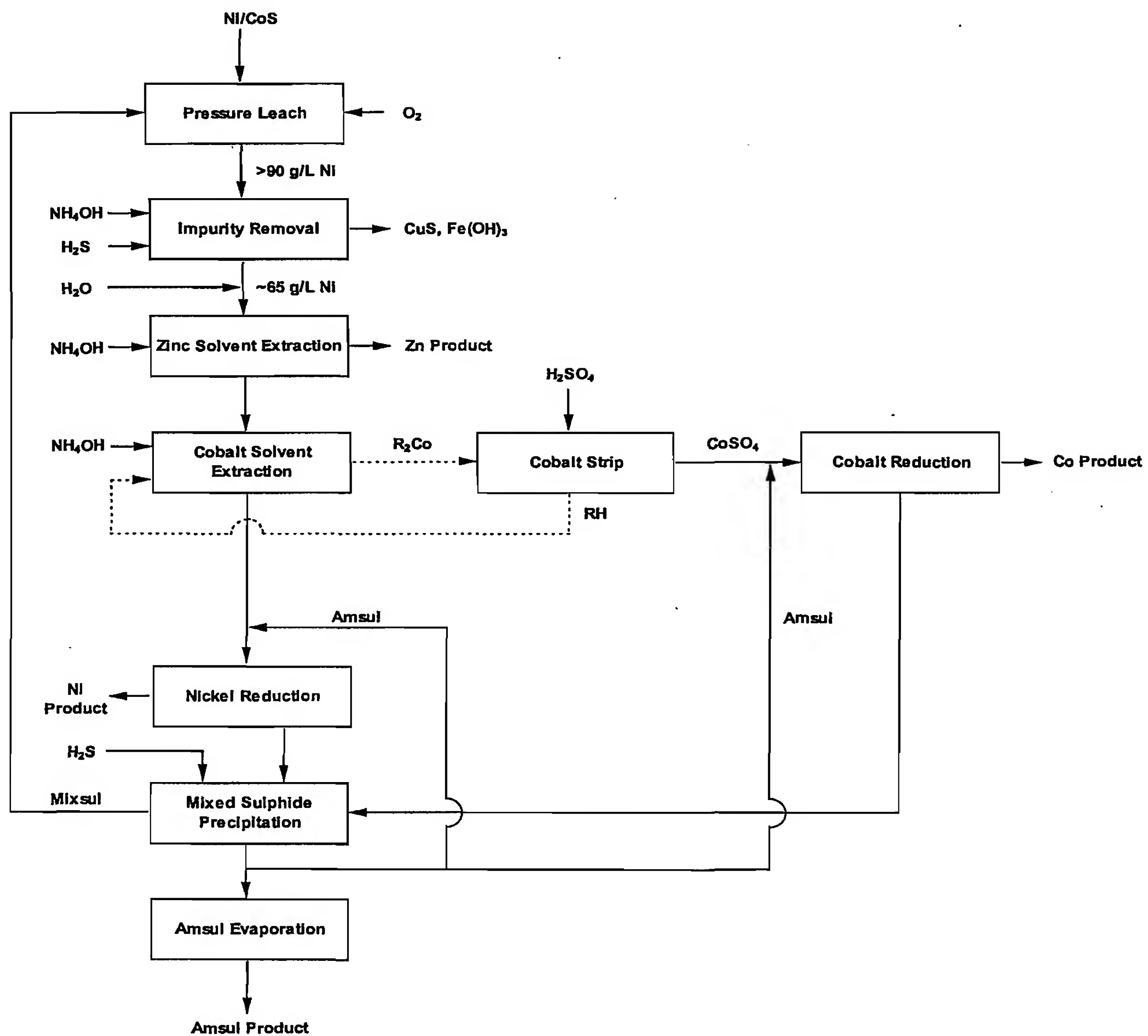


FIGURE 1

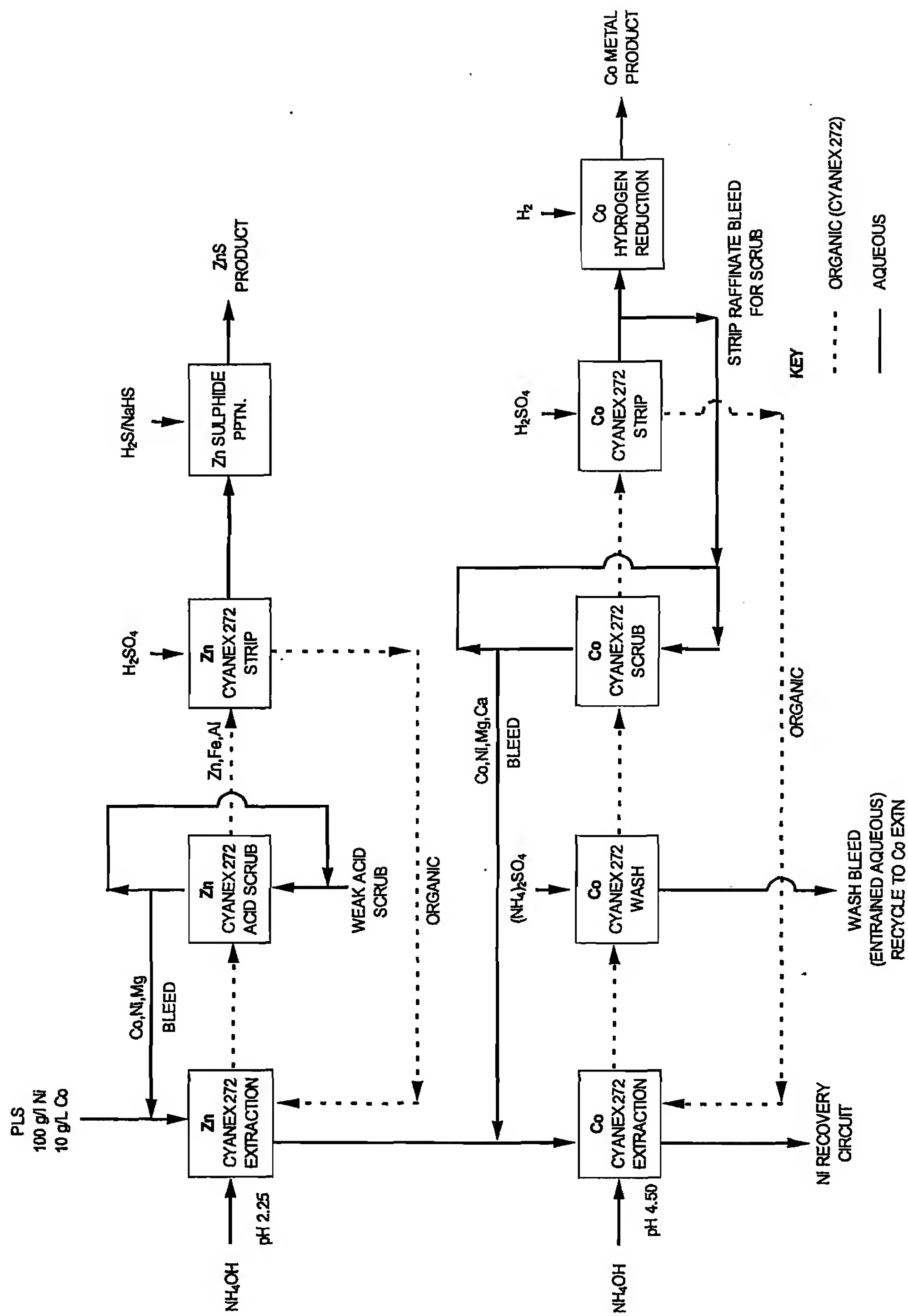


FIGURE 2

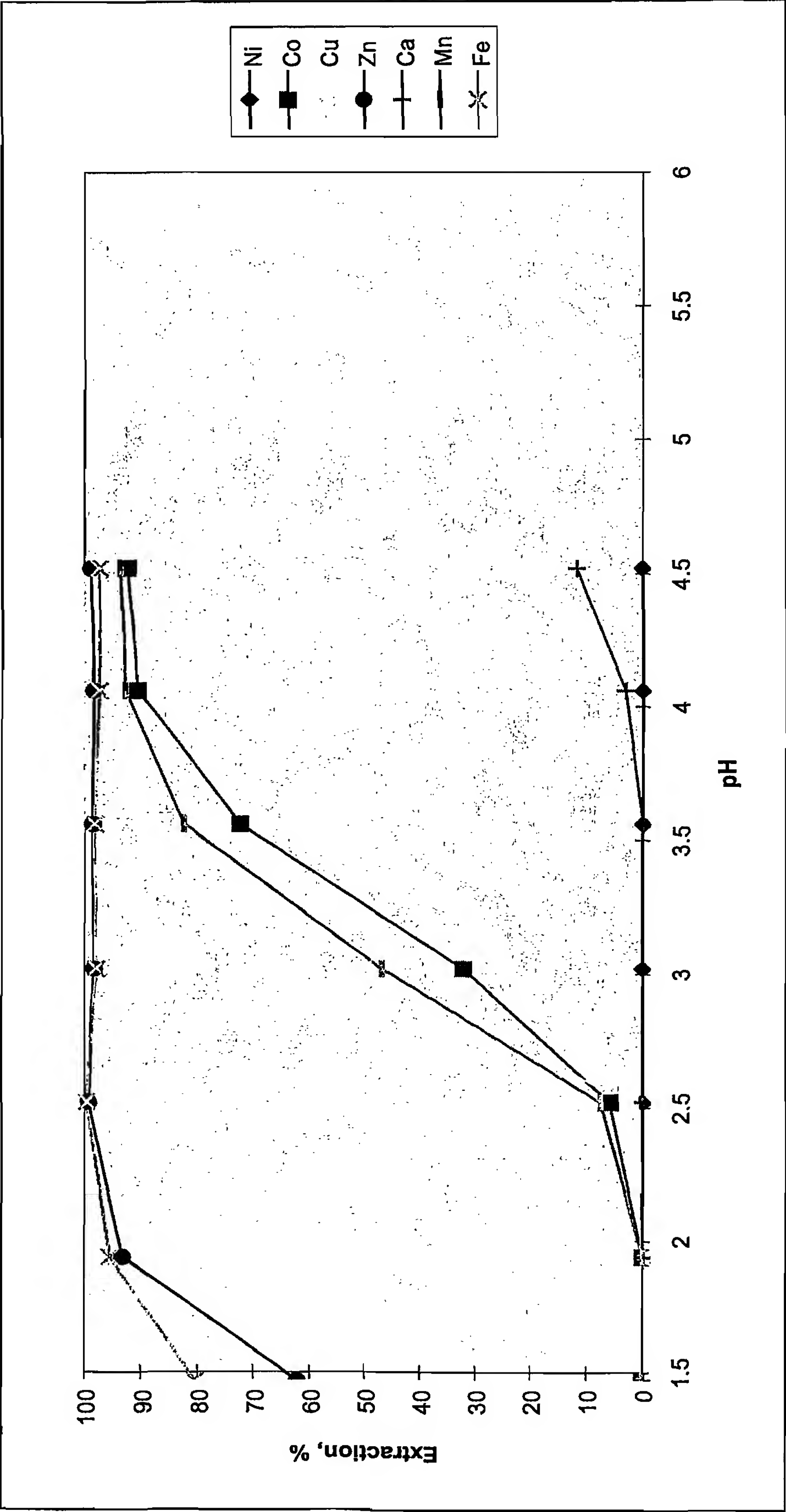


FIGURE 3

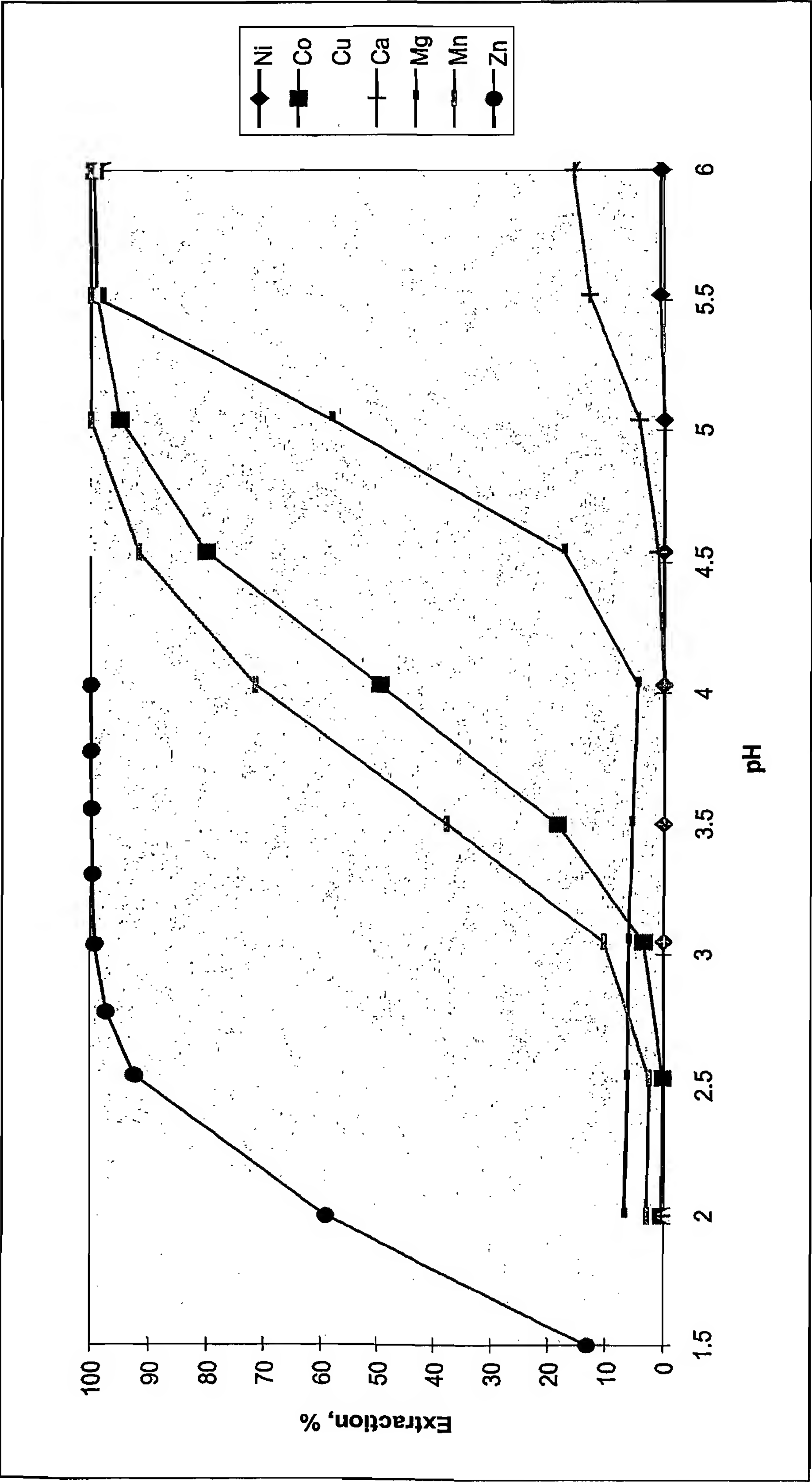


FIGURE 4

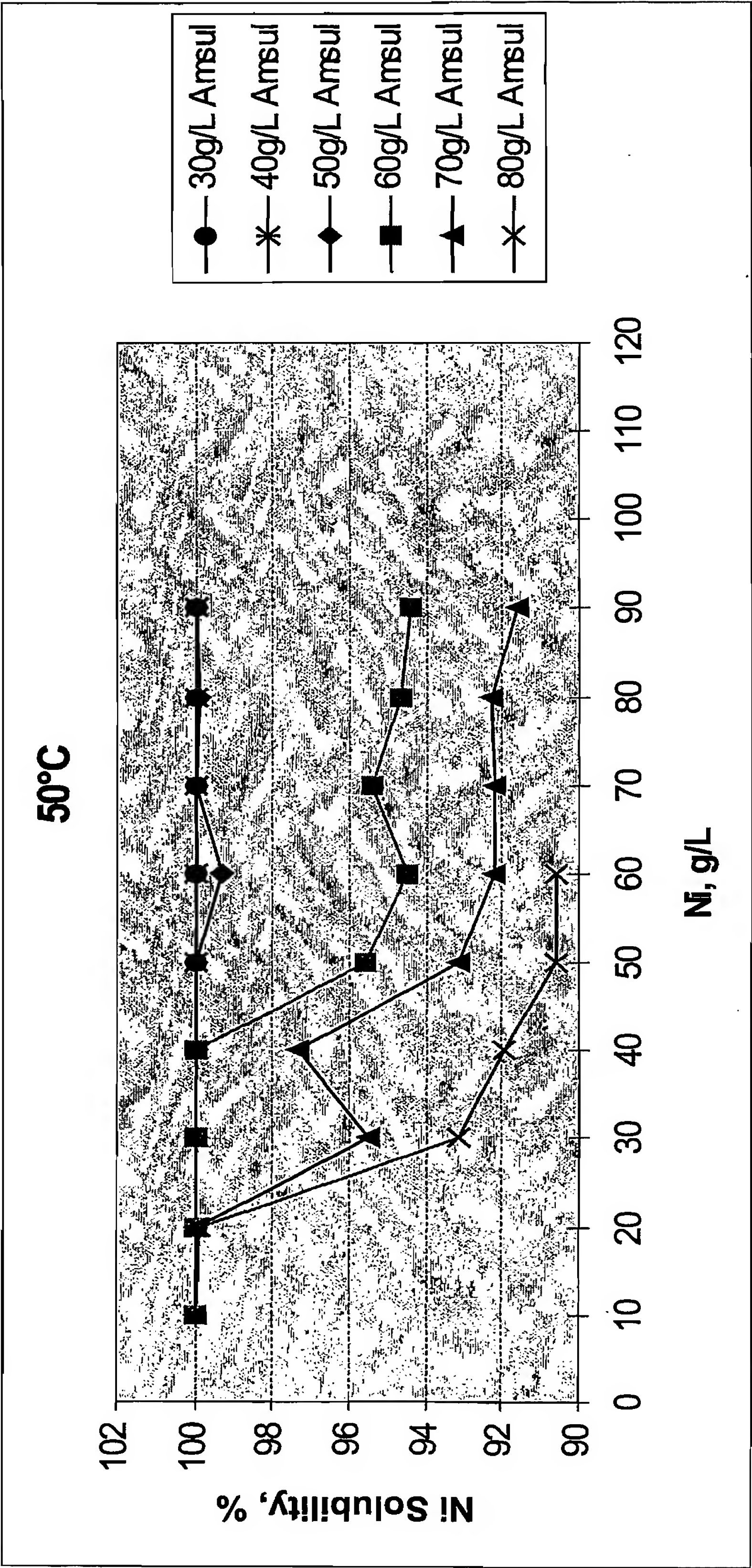


FIGURE 5

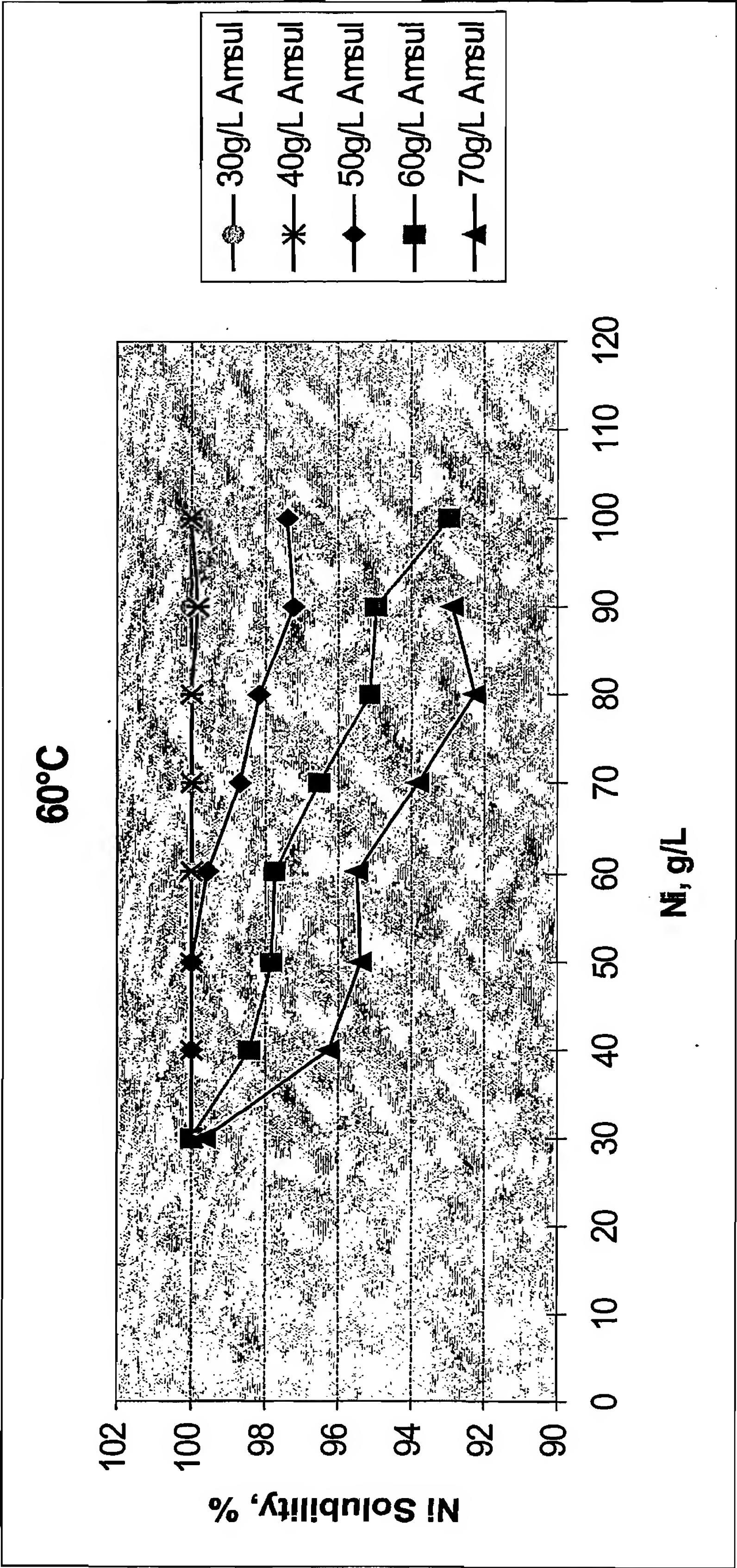


FIGURE 6

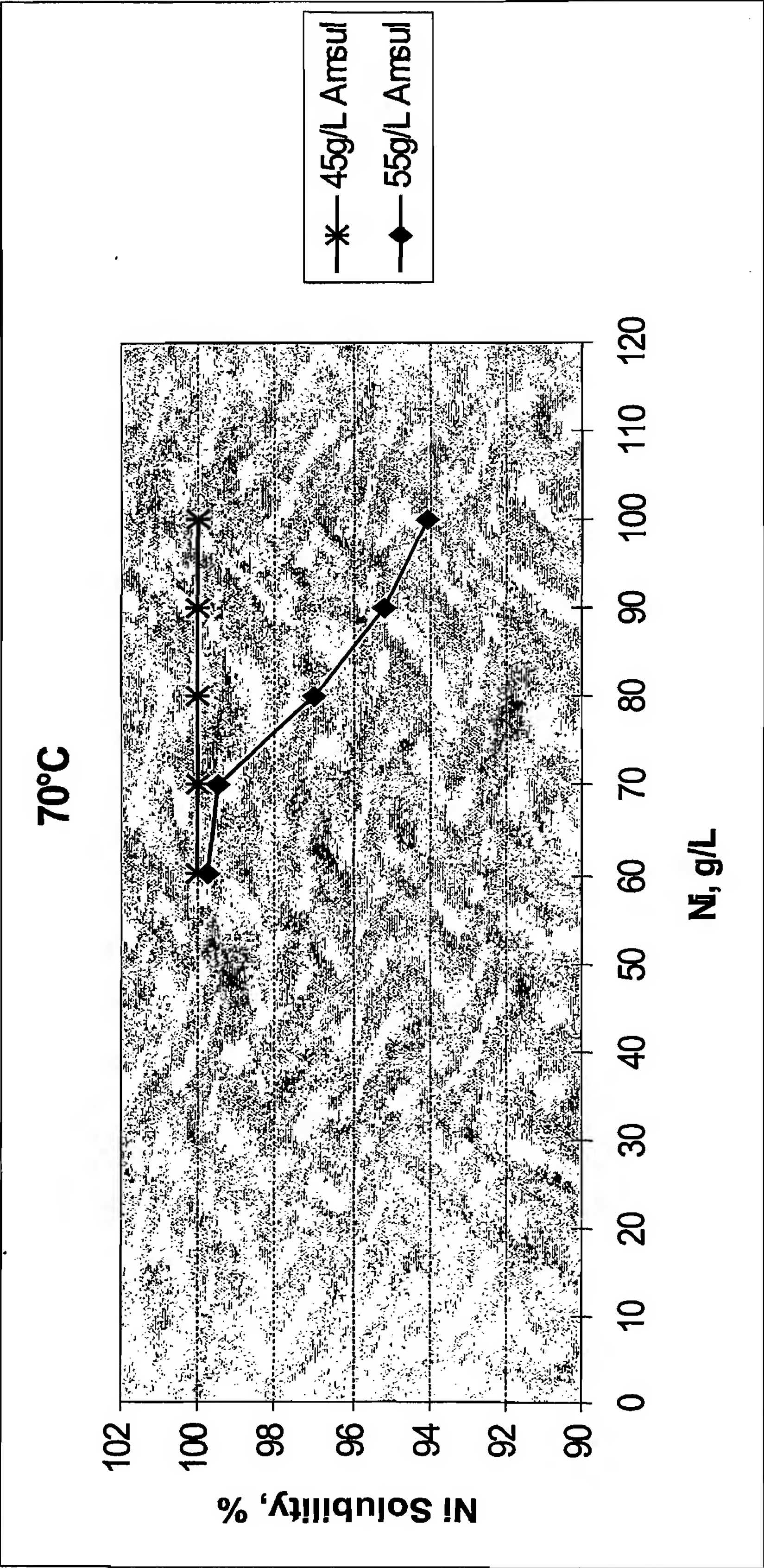


FIGURE 7

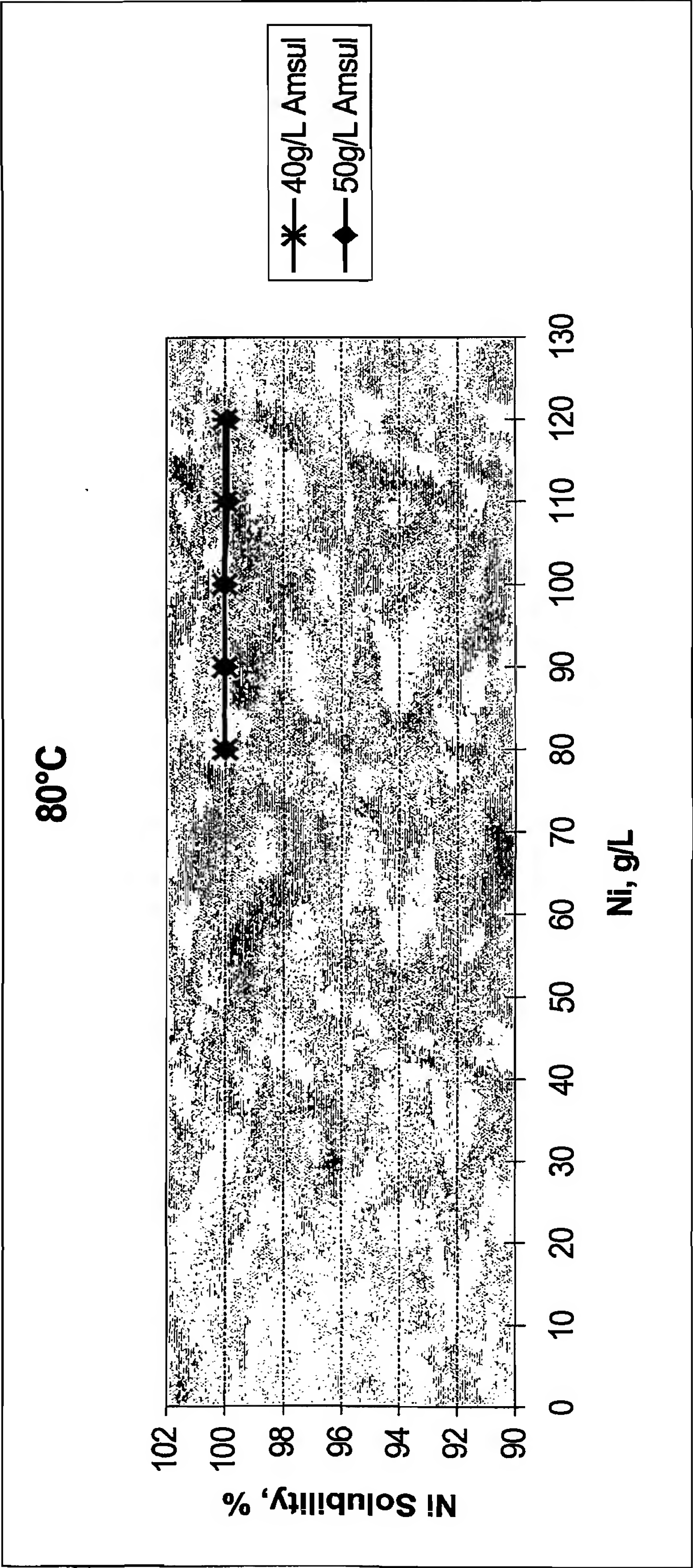


FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/00696

A. CLASSIFICATION OF SUBJECT MATTER																						
Int. Cl. ⁷ : C22B 3/26, 3/38, 3/40, 19/00, 23/00																						
According to International Patent Classification (IPC) or to both national classification and IPC																						
B. FIELDS SEARCHED																						
Minimum documentation searched (classification system followed by classification symbols) IPC C22B 3/26, 3/38, 3/40, 19/00, 23/00, 3/00, 23/04, 19/24, 19/26																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI IPC + (SULFATE SULPHATE) (AMMONI:)																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
A	WO 01/48252 A (WMC RESOURCES LIMITED) 5 July 2001																					
A	WO 98/56482 A (WMC RESOURCES LIMITED) 17 December 1998																					
A	CA 1024751 A (AMAX INC) 24 January 1978																					
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex																						
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E"</td> <td>earlier application or patent but published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L"</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	document published prior to the international filing date but later than the priority date claimed		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																			
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																			
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																			
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family																			
"P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 8 August 2001		Date of mailing of the international search report 17 AUGUST 2001																				
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer R.P. ALLEN Telephone No : (02) 6283 2134																				

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/00696

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2324792 A (SUMITOMO METAL MINING COMPANY LIMITED) 4 November 1998	
A	US 5855858 A (JONES) 5 January 1999	
A	US 5779997 A (NYMAN et al.) 14 July 1998	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU01/00696

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
WO	200148252	NONE					
WO	9856482	AU	80039/98				
CA	1024751	AU	76945/74	DE	2501395	FR	2260624
		JP	50115115	US	3933975	ZA	7500026
US	5855858	AU	61713/99	EP	804624	US	5431788
		US	5645708	US	5650057	US	5869012
		US	5874055	US	5902474	US	6054105
		WO	9619593	CA	2208026	AU	42960/96
		AU	44766/96	AU	58889/96	BG	102132
		BG	102133	BG	102149	BR	9608624
		BR	9608483	BR	9608499	CA	2221781
		CA	2221930	CA	2221940	CN	1186523
		CN	1186524	CN	1187220	EP	832302
		EP	832303	EP	832306	EP	924307
		EP	930373	FI	974427	FI	974428
		NO	975707	PL	323593	PL	323782
		PL	323799	WO	9641026	WO	9641027
		WO	9641029	ZA	9604866	BA	95051
		TR	970069	AU	12701/95	BG	101726
		BR	9408639	CZ	9701849	FI	972663
		HR	950601	NO	972836	PL	320939
		ZA	9410363	ZA	9510710	CA	2099333
GB	2324792	CA	2236125	JP	10310435	US	6149885
		JP	10310437				
US	5779997	AU	41267/93	CA	2098638	DE	4320314
		FI	922842	JP	7070656	NO	932223
		ZA	9304326	ZW	76/93		
END OF ANNEX							